ChemistrySELECT

Supporting Information

Reanalysis of the Much Referenced Ethanol-trichloromethane Mixture Vapor Pressure Data: A Discussion of the Principal Association Species Present

Stanley L. Manatt*

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Table S1. Comparison of SR's experimental mixture VP data with the MF's and *P*'s taken from enlarged copies the plots in Figure 4 of Raymond's thesis. Points fitted at 308.150 K. Pressures in mm Hg; ethanol MF.

MF	*P* (thesis and paper)	MF(off plot)	*P* (off plot)	ΔMF	Δ*P*
0.0384	303.91				
0.0400	303.69	First three data points were not plotted.			
0.0414	304.17				
0.0440	304.87	0.0441	304.44	+0.0001	-0.43
0.0685	306.05	0.0687	306.25	+0.0002	+0.20
0.1517	306.25	0.1497	306.05	-0.0020	-0.20
0.1577	305.12	0.1591	305.44	+0.0014	+0.32
0.1735	305.39	0.1737	305.29	+0.0002	-0.10
0.2254	303.05	0.2252	303.02	-0.0002	-0.03
0.3217	296.93	0.3220	296.98	+0.0003	-0.25
0.3816	291.95	0.3820	291.19	+0.0005	-0.76
0.5154	274.46	0.5149	274.80	-0.0005	+0.34
0.5173	274.04	Not plotted			
0.5616	267.65	Not plotted			
0.6078	255.28	0.6071	256.03	-0.0007	+0.75
0.6155	253.39	0.6146	254.14	-0.0009	+0.75
0.6773	236.50	0.6774	236.43	-0.0001	-0.03
0.6986	229.24	0.6984	229.49	-0.0002	+0.25
0.7127	225.06	0.7118	225.10	-0.0009	+0.04
0.7639	205.68	0.7630	205.62	-0.0009	-0.03
0.8270	177.60	0.8271	177.73	+0.0001	+0.13
0.8891	148.26	0.8887	149.20	-0.0004	+0.94
0.9406	125.82	0.9405	126.21	-0.0001	+0.39
0.9458	123.54	0.9468	123.54	+0.010	+0.02
0.9703	113.61	0.9706	114.05	+0.0003	+0.44
0.9759	111.31	0.9770	111.49	+0.0011	+0.18
0.9938	104.87	0.9955	104.81	+0.0017	-0.06
SSD[a]	4.6776		0.3547		

[a] Sum of the squares of the pressure errors.

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Table S2. Comparison of SR's experimental mixture VP data with the MF's and *P*'s taken from enlarged copies the plots in Figure 4 of Raymond's thesis. Points fitted at 318.150 K. Pressures in mm Hg; ethanol MF.

MF	*P* (thesis and paper)	MF(off plot)	*P* (off plot)	ΔMF	Δ*P*
0.0134	439.89	0.0144	438.74	+0.0010	-1.15
0.0242	443.07	0.0251	442.69	+0.0009	-0.33
0.0323	445.38	0.0346	445.41	+0.0023	+0.03
0.0443	448.49	0.0453	448.30	+0.0010	-0.19
0.0837	453.76	Not plotted.			
0.0875	454.02	0.0.875	453.77	0.0000	-0.25
0.0900	454.54	0.0.906	455.12	+0.0006	+1.10
0.1148	455.79	0.1145	455.78	-0.0003	-0.01
0.1794	455.56	0.1845	455.93	+0.0051	+0.37
0.2852	448.17	0.2875	448.99	+0.0023	+0.82
0.3717	438.89	0.3723	440.17	+0.0006	+1.25
0.4595	425.28	0.4665	424.43	+0.0070	+0.15
0.4860	420.68	0.4862	421.19	+0.0002	+0.51
0.5561	403.91	0.5575	404.90	+0.0014	+0.99
0.5985	391.51	0.5984	392.40	-0.0001	+0.89
0.6702	365.07	0.6699	365.93	-0.0003	+086
0.6884	355.66	0.6903	356.61	-0.0019	+0.95
0.7431	329.62	0.7425	331.51	-0.0006	+1.89
0.7989	299.63	0.7985	299.32	-0.0004	-0.31
0.8003	298.08	0.8000	297.99	-0.0003	-0.09
0.8740	249.92	0.8753	249.88	+0.0013	-0.04
0.9288	214.44	0.9294	214.33	+0.0006	-0.11
0.9524	199.62	0.9632	199.83	+0.0008	+0.21
0.9811	182.63	0.9823	182.83	+0.0012	+0.20
0.9843	180.96	0.9850	181.00	+0.0007	-0.96
SSD[a]	5.2302		2.3344		

[a] Sum of the squares of the pressure errors.

Table S3. Comparison of SR's experimental mixture VP data with the MF's and *P*'s taken from enlarged copies the plots in Figure 4 of Raymond's thesis. Points fitted at 328.150 K. Pressures in mm Hg; ethanol MF.

MF	*P* (thesis and paper)	MF(off plot)	*P* (off plot)	ΔMF	Δ*P*
0.0348	626.79	0.0340	636.31	+0.0008	-9.52
0.0570	644.24	0.0560	643.18	-0.0010	-1.06
0.0963	650.38	0.0937	650.63	-.0.0026	+0.25
0.1610	653.11	0.1620	653.31	+0.0010	+0.20
0.2236	650.96	0.2232	650.63	-0.0004	-0.33
0.2731	646.79	0.2728	646.69	-0.0003	-0.10
0.3149	641.49	0.3136	641.60	-0.0013	+0.11
0.3789	632.14	0.3776	632.35	-0.0013	+0.21
0.4270	623.67	0.4264	623.33	-0.0006	-0.34
0.5206	599.03	0.5168	599.16	-0.0038	+0.13
0.6035	569.02	0.6016	568.91	-0.0019	-0.11
0.6096	566.74	0.6088	56638	-0.0008	-0.36
0.6233	560.25	0.6232	560.29	-0.0001	+0.04
0.6555	545.72	0.6536	545.36	-0.0019	-0.36
0.6588	543.53	0.6583	543.66	-0.0001	+0.89
0.7194	508.78	0.7200	509.26	+0.0006	+0.48
0.7788	469.41	0.7800	469.03	+0.0001	-0.38
0.8131	441.04	0.8128	442.15	-0.0003	+1.11
0.8521	407.90	0.8521	409.34	0.0000	+1.44
0.8971	367.01	0.8965	368.40	-0.0006	+1.39
0.9198	346.89	0.9200	347.05	+0.0002	+0.16
0.9288	339.89	0.9289	339.48	+0.0001	-0.41
0.9669	306.38	0.9678	306.74	+0.0009	+0.36
SSD[a]	5.2537		2.6938		

[a] Sum of the squares of the pressure errors.

Table S4. Three sets of fittings used to estimate temperatures to be used in final fittings to SR experimental data. See text for identification of parameters used in numbered fitting. All pressures in mm Hg. SSD is sum of squares of pressure errors.

T = 308.1500K

1 P_1 = 102.78 mm (308.0766 K), P_2 = 295.11 mm (308.0105 K) SSD = 5.6448
β_1 = -1090, $\beta_{2=}$ -1470, β_{12} = -1930; MV_1 = 61.4, MV_2 = 81.7

2 P_1 = 103.1860 mm (308.150 K), P_2 = 296.7477 mm (308.150 K) SSD = 7.5101
β_1 = -1090, $\beta_{2=}$ -1470, β_{12} = -1930; MV_1 = 61.4, MV_2 = 81.7

3 P_1 = 102.7550 mm (308.0721 K), P_2 = 295.4972 mm (308.0435 K) SSD = 5.4703
β_1 = -1090, $\beta_{2=}$ -1470, β_{12} = -1930; MV_1 = 61.4, MV_2 = 81.7

4 P_1 = 102.78 mm (308.0766 K), P_2 = 295.11 mm (308.0105 K) SSD = 5.5409
β_1 = -1479.92, $\beta_{2=}$ -1244.25, β_{12} = -1415.59; MV_1 = 59.53, MV_2 = 70.72

5 P_1 = 103.1860 mm (308.150 K), P_2 = 296.7477 mm (308.150 K) SSD = 7.5233
β_1 = -1479.92, $\beta_{2=}$ -1244.25, β_{12} = -1415.59; MV_1 = 59.53, MV_2 = 70.72

6 P_1 = 102.9578 mm (308.1088 K), P_2 = 297.1069 mm (308.1805 K) SSD = 4.6776
β_1 = -1479.92, $\beta_{2=}$ -1244.25, β_{12} = -1415.59; MV_1 = 59.53, MV_2 = 70.72

T = 318.1500K

1 P_1 = 172.76 mm (318.1122 K), P_2 = 433.54 mm (318.0871 K) SSD = 5.1547
β_1 = -960, $\beta_{2=}$ -1290, β_{12} = -1450; MV_1 = 62.2, MV_2 = 82.7

2 P_1 = 173.0855 mm (318.150 K), P_2 = 434.5420 mm (308.150 K) SSD = 5.9990
β_1 = -960, $\beta_{2=}$ -1290, β_{12} = -1450; MV_1 = 62.2, MV_2 = 82.7

3 P_1 = 172.6608 mm (318.1007 K), P_2 = 433.2342 mm (318.0679 K) SSD = 5.1073
β_1 = -960, $\beta_{2=}$ -1290, β_{12} = -1450; MV_1 = 62.2, MV_2 = 82.7

4 P_1 = 172.76 mm (318.1122 K), P_2 = 433.54 mm (318.0871 K) SSD = 5.3299
β_1 = -1301.81, $\beta_{2=}$ -1120.85, β_{12} = -11255.63; MV_1 = 60.34, MV_2 = 70.89

5 P_1 = 173.0855 mm (318.150 K), P_2 = 434.5420 mm (308.150 K) SSD = 6.2602
β_1 = -1301.81, $\beta_{2=}$ -1120.85, β_{12} = -11255.63; MV_1 = 60.34, MV_2 = 70.89

6 P_1 = 172.6583 mm (318.1005 K), P_2 = 433.1485 mm (318.0619 K) SSD = 5.2537
β_1 = -1479.92, $\beta_{2=}$ -1244.25, β_{12} = -1415.59; MV_1 = 59.53, MV_2 = 70.72

T = 318.1500K

1 P_1 = 279.86 mm (328.1378 K), P_2 = 617.84 mm (328.1034 K) SSD = 6.9997
β_1 = -865, $\beta_{2=}$ -1150, β_{12} = -1170; MV_1 = 62.8, MV_2 = 83.8

2 P_1 = 280.0189 mm (328.150 K), P_2 = 618.8215 mm (308.150 K) SSD = 7.6677
β_1 = -960, $\beta_{2=}$ -1290, β_{12} = -1450; MV_1 = 62.2, MV_2 = 82.7

3 P_1 = 282.3870 mm (328.3315 K), P_2 = 620.0872 mm (328.2100 K) SSD = 5.2547
β_1 = -960, $\beta_{2=}$ -1290, β_{12} = -1450; MV_1 = 62.2, MV_2 = 82.7

4 P_1 = 279.86 mm (328.1378 K), P_2 = 617.84 mm (328.1034 K) SSD = 6.9405
β_1 = -1154.21, $\beta_{2=}$ -1017.17, β_{12} = -1122.61; MV_1 = 61.18, MV_2 = 71.06

5 P_1 = 280.0189 mm (328.150 K), P_2 = 618.8215 mm (308.150 K) SSD = 7.6416
β_1 = -1154.21, $\beta_{2=}$ -1017.17, β_{12} = -1122.61; MV_1 = 61.18, MV_2 = 71.06

6 P_1 = 172.6583 mm (318.1005 K), P_2 = 433.1485 mm (318.0619 K) SSD = 5.2537
β_1 = -1154.21, $\beta_{2=}$ -1017.17, β_{12} = -1122.61; MV_1 = 61.18, MV_2 = 71.06

Table S5. An exhibit of the discrepancies between g_X^E's calculated in Raymonds thesis and the values given in the published SR paper. The discrepancies are shown in bold. Recalculations in the present work arrived at the same values as in Raymond's thesis. Units of joules per mole.

	35° C		45° C		55° C	
MF **1**	Paper	Thesis	Paper	Thesis	Paper	Thesis
0.01	45	45.4	44	44.2	38	38.5
0.02	88	88.6	83	**84.1**	79	**80.1**
0.05	203	**204.3**	196	**204.3**	188	**189.8**
0.10	358	**359.0**	357	**358.0**	337	**339.1**
0.20	564	**565.0**	575	575.7	554	**556.5**
0.30	669	668.5	686	685.8	672	**674.2**
0.40	699	698.2	722	721.3	716	716.5
0.50	657	**654.5**	691	**689.6**	686	**687.8**
0.60	568	**565.6**	600	**598.4**	611	**612.2**
0.70	425	**422.2**	468	**466.0**	485	**486.0**
0.80	265	**263.4**	311	**309.9**	335	**337.3**
0.90	129	**119.2**	147	146.5	164	164.8
0.95	52	52.1	74	73.7	77	77.8
0.98	21	20.9	27	26.9	30	30.1
0.99	11	11.2	12	11.7	15	15.2
Number of Discrepancies		8		7		9

Table S6. Activity coefficients of **2** as a function of **2** MF.

	Temperatures Degrees K			
MF	298.150	308.150	318.150	328.150
1.00	1.0000	1.0000	1.0000	1.0000
0.99	1.0003	1.0019	1.0009	1.0010
0.98	1.0009	1.0037	1.0025	1.0024
0.95	1.0050	1.0089	1.0102	1.0088
0.90	1.0193	1.0302	1.0327	1.0273
0.80	1.0764	1.1016	1.1053	1.0896
0.70	1.1676	1.2017	1.2043	1.1791
0.60	1.2862	1.3241	1.3233	1.2890
0.50	1.4253	1.4647	1.4592	1.4164
0.40	1.5738	1.6142	1.6059	1.5591
0.30	1.7040	1.7476	1.7442	1.7061
0.20	1.7456	1.8102	1.8287	1.8156
0.10	1.5735	1.7157	1.7830	1.7887
0.05	1.3702	1.5830	1.6846	1.6796
0.02	1.2111	1.4736	1.5973	1.5748
0.01	1.1529	1.4323	1.5634	1.5331
0.00	1.0926	1.3889	1.5273	1.4881

Table S7. Activity Coefficients of **1** as a Function of **1** MF.

	Temperatures Degrees K			
MF	298.150	308.150	318.150	328.150
0.00	3.9048	5.4412	5.6463	4.4259
0.01	3.7679	5.0892	5.2623	4.2137
0.02	3.6352	4.7717	4.9178	4.0160
0.05	3.2644	3.9880	4.0772	3.4996
0.10	2.7399	3.0833	3.1255	2.8447
0.20	2.0022	2.0902	2.1088	2.0375
0.30	1.5617	1.6003	1.6195	1.6016
0.40	1.2994	1.3296	1.3515	1.3509
0.50	1.1413	1.1691	1.1919	1.1976
0.60	1.0469	1.0729	1.0939	1.1003
0.70	0.9964	1.0200	1.0370	1.0402
0.80	0.9802	0.9985	1.0097	1.0092
0.90	0.9889	0.9976	1.0000	1.0006
0.95	0.9967	1.0000	1.0017	1.0008
0.98	0.9997	1.0005	1.0010	1.0008
0.99	1.0001	1.0004	1.0006	1.0005
1.00	1.0000	1.0000	1.0000	1.0000

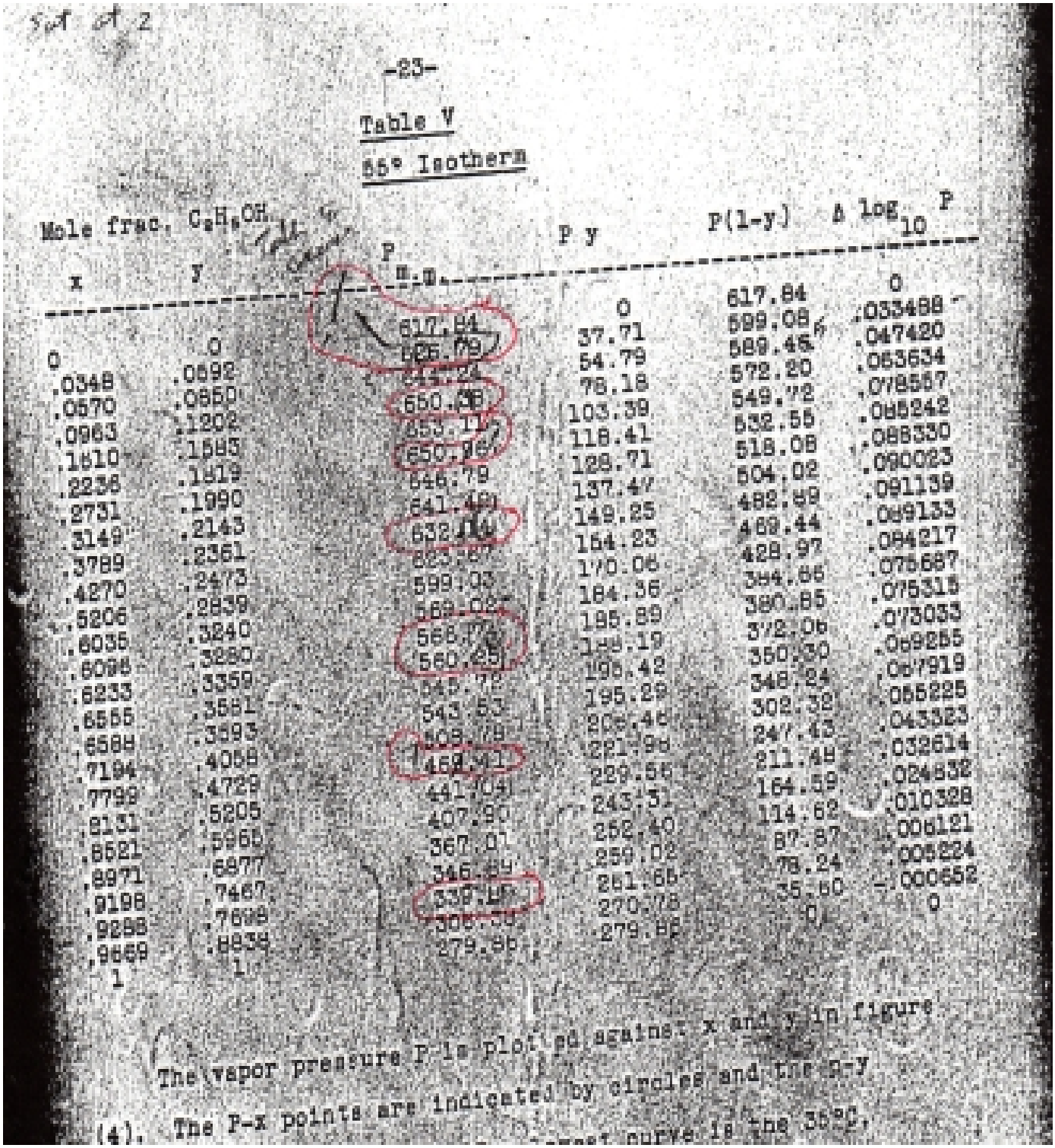

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Table V

55° Isotherm

Mole frac. C_2H_5OH.		P	P y	P(1-y)	Δ log$_{10}$ P
x	y	m.m.			
0	0	617.84	0	617.84	0
.0348	.0692	605.79	37.71	599.08	.033488
.0570	.0850	614.24	54.79	589.46	.047420
.0963	.1202	650.98	78.18	572.20	.063634
.1610	.1585	653.12	103.39	549.72	.078567
.2236	.1819	650.96	118.41	532.55	.088242
.2731	.1990	646.79	128.71	518.08	.098330
.3149	.2143	641.48	137.47	504.02	.090023
.3789	.2361	632.14	149.25	482.89	.091139
.4270	.2473	623.87	154.23	468.44	.089133
.5206	.2839	599.03	170.06	428.97	.084217
.6036	.3240	569.02	184.36	384.66	.075687
.6098	.3280	568.77	186.89	380.85	.075315
.6233	.3359	560.25	188.19	372.06	.073033
.6555	.3561	545.72	196.42	350.30	.069255
.6588	.3693	543.83	201.98	348.24	.067919
.7194	.4058	503.79	204.46	302.32	.055225
.7799	.4729	468.41	221.98	247.43	.043323
.8131	.5205	441.04	229.56	211.48	.032614
.8521	.5965	407.90	243.31	164.59	.024832
.8971	.6877	367.01	252.40	114.62	.010328
.9198	.7467	346.84	259.02	87.87	.006121
.9288	.7699	338.10	261.66	78.24	.005224
.9669	.8838	306.30	270.78	35.60	-.000652
1	1	279.86	279.86	0	0

The vapor pressure P is plotted against x and y in figure (4). The P-x points are indicated by circles and the P-y [illegible] curve is the 35°C.

Figure S1. A copy of a weathered photostat of part of page 23 of Raymond's thesis [7] with hand written changes (circled in red) to the VP's at 55° C.